

Moving excitons in graphene

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(Dated: March 3, 2013)

We demonstrate the possibility of existence of indirect moving excitons in graphene. The binding is conditioned by the trigonal warping of conic energy spectrum. The binding energies are found for the lowest exciton states. These energies essentially depend on the value and direction of exciton momentum and vanish when the exciton momentum tends to the conic points. The ways to observe the exciton states are discussed. It is shown that the statistics of graphene at finite temperature experiences corrections caused by the exciton states.

PACS numbers: 71.35.-y, 73.22.Lp, 73.22.Pr, 78.67.Wj, 65.80.Ck

Introduction. Graphene is a remarkable material due to its unusual conic electron energy spectrum. One of the important consequences of this singularity is zero effective mass of electrons near the conic point that results in a high potential mobility of charge carriers in graphene. Just this fact makes graphene very perspective for electronics. Another important property of free-suspended graphene is potentially large dimensionless interaction constant that strongly distorts a single-particle spectra.

The purpose of the present paper is an envelope-approximation study of possibility of the Wannier-Mott excitons formation near the conic point in a neutral graphene. There were a lot of studies considered the excitons in graphene. Unlike the present paper, the term "exciton" in all these papers is used for many-body ("excitonic") effects^{1,2}, exciton insulator with full spectrum reconstruction, or exciton-like singularities originating from saddle points (van Hove singularity) of the single-particle spectrum³ where the real electron-hole binding does not occur. On the contrary, our goal is pair bound states of electrons and holes. There is widely accepted opinion that zero gap in graphene forbids the Mott exciton states (see, i.g.,⁴). This statement valid in the conic approximation proves to be incorrect beyond this approximation. It will be shown that exciton existence is conditioned by the trigonal corrections to the conic spectrum.

The trigonal warping of the energy spectrum is responsible for the electron-electron scattering selection rules in the neutrality point and, consequently, a specific mechanism of the valley currents in graphene⁵. Here we shall demonstrate that the presence of the warping drastically affects the possibility of electron-hole binding also.

We consider graphene with weakly interacting charged carriers, when the interaction constant $g = e^2/v\chi \ll 1$, where e is electron charge, v is electron velocity in the conic approximation, χ is the half-sum of dielectric constants of surrounding media, $\hbar = 1$. First, let us discuss the behavior of a classical electron-hole pair with conic spectra vp . Let electrons and holes have parallel momenta. Due to equality of velocities, the distance between e and h remains constant. The interaction between them changes the momenta but does not change their distance. This behavior strongly differs from a usual pair

with quadratic spectra where the interaction produces a well in which e and h oscillate. The quantum counterpart of this oscillation is an e - h pairing. Beyond the conic approximation the series expansion of the pair kinetic energy in the momentum determines the finite inverse mass (second derivative of energy with respect to the momentum) that leads to the variation of the e - h distance. However, the oscillations occur only if the sign of this mass is positive. Below, we demonstrate that this sign depends on the momentum angle, that means the binding exists in particular sectors of the momentum space and is forbidden in others.

Exciton states. We start from the tight-binding electron Hamiltonian

$$H_e(\mathbf{p}) = \begin{pmatrix} 0 & \Omega_{\mathbf{p}} \\ \Omega_{\mathbf{p}}^* & 0 \end{pmatrix}, \quad \Omega_{\mathbf{p}} = -\gamma \sum_i e^{-i\mathbf{p}\mathbf{b}_i}, \quad (1)$$

where $\gamma = 2v/a\sqrt{3}$, $b_1 = (0, 1)a/\sqrt{3}$, $b_2 = (-3, -\sqrt{3})a/6$, $b_3 = (3, -\sqrt{3})a/6$, $a = 0.246$ nm is the lattice constant. The spectrum reads as

$$\varepsilon_{\pm}(\mathbf{p}) = \pm\gamma\sqrt{1 + 4\cos\frac{ap_x}{2}\cos\frac{\sqrt{3}ap_y}{2} + 4\cos^2\frac{ap_x}{2}}.$$

We will consider the case when the binding is weak and the exciton states are composed from the narrow group in the momentum space. Near points K and K' , where $\mathbf{p} = \pm\mathbf{K}$, $\mathbf{K} = (1, 0)4\pi/3a$, the spectrum is conic: $\varepsilon_{\pm}(\mathbf{p}) = \pm v|\mathbf{p} - \mathbf{K}|$ and $\varepsilon_{\pm}(\mathbf{p}) = \pm v|\mathbf{p} + \mathbf{K}|$, correspondingly. In the envelope approximation the two-body Hamiltonian is

$$H_{ex} = H_e(\mathbf{p}_e) \otimes I_h - I_e \otimes H_h(\mathbf{p}_h) + I_e \otimes I_h V(\mathbf{r}_e - \mathbf{r}_h), \quad (2)$$

where $H_h(\mathbf{p}) = -H_e(-\mathbf{p})$ is the hole Hamiltonian, $\mathbf{r}_{e,h}$ and $\mathbf{p}_{e,h}$ are electron and hole coordinates and momenta, $V(\mathbf{r}) = -e^2/\chi r$ is the potential of electron-hole interaction. The electron and hole Hamiltonians relate to the electron and hole subspaces of quantum numbers. Hamiltonian (2) has a 4-fold set of states, one of which belongs to the ordinary exciton, namely, a pair with "an electron in the conduction band and a hole in the valence band".

Let us carry out the unitary transform $U = U_e(\mathbf{p}_e)U_h(\mathbf{p}_h)$ of the Hamiltonian (2), where $U_e(\mathbf{p}_e)$ and $U_h(\mathbf{p}_h)$ diagonalize $H_e(\mathbf{p}_e)$ and $H_h(\mathbf{p}_h)$, respectively. The smallness of the binding energy means large size

of exciton wave function and the smallness of the spatial derivatives; in that case one can neglect the non-commutativity of U and $V(\mathbf{r}_e - \mathbf{r}_h)$. As a result, we get to the Hamiltonian:

$$H = \varepsilon_+(\mathbf{p}_e) + \varepsilon_+(\mathbf{p}_h) + V(\mathbf{r}_e - \mathbf{r}_h). \quad (3)$$

The electron and hole momenta can be expressed via pair $\mathbf{q} = \mathbf{p}_e + \mathbf{p}_h$ and relative $\mathbf{p} = \mathbf{p}_e - \mathbf{p}_h$ momenta. The momenta can be situated near the same ($q \rightarrow k \ll 2K$) or near the opposite conic points ($\mathbf{q} = 2\mathbf{K} + \mathbf{k}$, $k \ll 2K$) (see Fig. 1).

Further simplifications are done assuming that the binding energy of the pair is less than kinetic energy vk . The result is the Schrödinger Hamiltonian

$$H_{ex} = vk + \frac{p_1^2}{2M} + \frac{p_2^2}{2m} - \frac{e^2}{\chi r}, \quad (4)$$

where the coordinate system with basis vectors $\mathbf{e}_1 \equiv \mathbf{k}/k$ and $\mathbf{e}_2 \perp \mathbf{e}_1$ is chosen. In the conic approximation we have $m = k/v$, $M = \infty$. To obtain finite M , one should go beyond the conic approximation. For the indirect exciton (electron and hole from different cones) with the momenta close to $\nu 2\mathbf{K}$, ($\nu = \pm 1$), we have $1/M = \nu va \cos(3\phi_{\mathbf{k}})/4\sqrt{3}$, where $\phi_{\mathbf{k}}$ is an angle between \mathbf{k} and \mathbf{K} . Effective mass M is directly determined by the trigonal contributions to the spectrum and is parametrically large: $\eta = M/m = 4\sqrt{3}/(\nu ka \cos 3\phi_{\mathbf{k}}) \gg 1$. The sign of M is determined by $\nu \cos 3\phi_{\mathbf{k}}$. If $\nu \cos 3\phi_{\mathbf{k}} > 0$, electron and hole tend to bind, otherwise to run away from each other. Thus, the binding is possible for $\nu \cos 3\phi_{\mathbf{k}} > 0$.

The similar reasoning for the pair from the same valley shows that the trigonal contributions to $1/M$ cancel each other. The contributions of a higher order give, in this case, a negative mass $1/M$: $1/M = -kva^2(7 - \cos 6\phi_{\mathbf{k}})/32$. As a result, the electron-hole binding is forbidden for particles from the same valley.

The indirect exciton existence needs, positively definiteness of the effective mass tensor. The corresponding condition valid apart from the conic point reads

$$(1 + s + t_-)(1 + s + t_+)(1 + t_- + t_+) > 0, \quad (5)$$

where $s = \cos ak_x$, $t_{\pm} = \cos((k_x \pm \sqrt{3}k_y)a/2)$.

Fig. 1 shows the domain of exciton existence in the momentum space. This domain covers a small part of the Brillouin zone.

The problem of Coulomb states for the Hamiltonian (4) can be considered using strong anisotropy of the energy spectrum. The kinetic energy of the free pair vk is the main part of the exciton energy $vk - \varepsilon_{nN}$, where $\varepsilon_{nN} > 0$ is the binding energy, quantum numbers n and N numerate the exciton state. A large ratio of masses $\eta \gg 1$ reminds of the problem of molecular states, where m and M represent electron and ion masses, correspondingly. So the way of solution is similar to the problem of molecular levels. First, we cancel $p_1^2/2M$, fix the "ion" coordinate "x" and determine the energy terms $vk - \varepsilon_n(x)$, then use these terms as ions potential energy. The binding energy

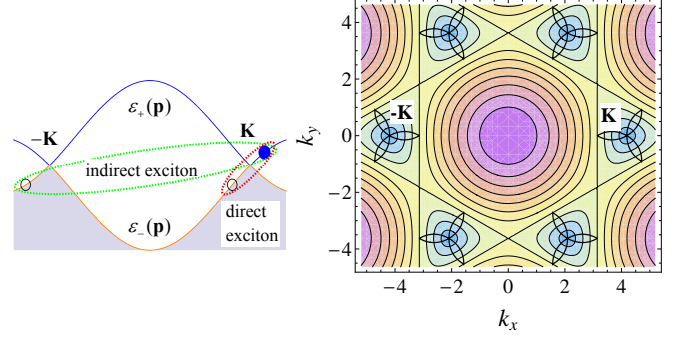


FIG. 1. Left: Direct and indirect exciton formation in terms of single-particle spectrum. Right: Relief of the single-electron spectrum. Energy runs from 0 in the conic points to 3γ in the center. The trefoils bound the permitted domains of $\mathbf{q}/2$ for indirect exciton momentum \mathbf{q} .

ε_{nN} in the N-th "ion" state on the n-th "electron" term is determined by the Schrödinger equation for "ions"

$$(p_1^2/2M - \varepsilon_n(x) + \varepsilon_{nN}) \Psi_{nN}(x) = 0. \quad (6)$$

The order of magnitude of the lowest levels is the Bohr energy $\epsilon_B = me^4/\chi^2$.

Let us replace the potential of electron-hole interaction by $V(\mathbf{r}) \simeq -e^2/\chi(|x| + |y|)$ which has the same asymptotics. This approach permits to approximate the energy terms at small y ($y \ll x$). The replacement converts the Schrödinger equation to the analytically solvable one:

$$\frac{1}{2m} \psi''(y) + \frac{e^2}{\chi(|y| + |x|)} \psi(y) = \varepsilon(x) \psi(y). \quad (7)$$

The solution of Eq. (7) satisfying zero boundary condition at $|y| \rightarrow \infty$ ($\varepsilon(x) > 0$) is

$$\psi(y) = C_{\pm} e^{-P(x)(|y| + |x|)} (|y| + |x|) \cdot U[1 - (P(x)a_B)^{-1}, 2, 2P(x)(|y| + |x|)], \quad (8)$$

where $a_B = \chi/me^2$ is the Bohr radius, $U[a, b, z]$ is the confluent hypergeometric function, $P(x) = \sqrt{2m\varepsilon(x)}$, coefficients C_{\pm} correspond to $y > 0$ and $y < 0$ domains. Even and odd solutions satisfy the boundary condition $\psi'_{even}(0) = 0$ and $\psi_{odd}(0) = 0$, accordingly. This gives the energy terms at $x \ll a_B$: $\varepsilon_0(x) = 2\epsilon_B \log^2 \frac{a_B}{|x|}$,

$$\varepsilon_n^{even}(x) \approx \frac{\epsilon_B}{2n^2} - \frac{\epsilon_B}{n^3 \log \frac{a_B}{|x|}}, \quad (9)$$

$$\varepsilon_n^{odd}(x) \approx \frac{\epsilon_B}{2n^2} - \frac{2\epsilon_B |x|}{n^3 a_B}, \quad (10)$$

where $n \geq 1$. Using the energy terms and Eq. (6) we obtain the energy levels in the quasiclassical approximation:

$$\varepsilon_{00} \approx (\epsilon_B/2) \log^2 \eta + \dots, \quad (11)$$

$$\varepsilon_{nN}^{even} \approx \frac{\epsilon_B}{2n^2} - \frac{2\epsilon_B}{n^3 \eta \log \frac{2\eta}{\pi^2 n^3 (N + \frac{1}{4})}} + \dots, \quad (12)$$

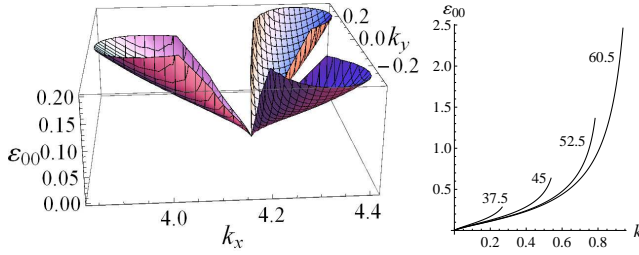


FIG. 2. Left: Binding energy (in eV) of the ground state of indirect exciton in graphene *versus* wave vector in units of reciprocal lattice constant. Exciton exists in the sectors shown in left figure. Right: Radial sections of right figure at fixed angles in degrees (marked). Curves run up to the ends of exciton spectrum.

$$\varepsilon_{nN}^{odd} \approx \frac{\epsilon_B}{2n^2} - \frac{\epsilon_B}{n^2} \left[\frac{3\pi}{4\eta^2} \left(N + \frac{3}{4} \right) \right]^{\frac{2}{3}} + \dots \quad (13)$$

The distance between "ions" levels $\varepsilon_{n,N+1} - \varepsilon_{n,N}$ is much less, than the distance between "electron" levels $\varepsilon_{n+1,N} - \varepsilon_{n,N}$ by measure of the parameter $1/\eta$.

Application of the variational approach to the Hamiltonian (4) with full variational wave functions $\exp(-x^2/a_x^2 - y^2/a_y^2)$ and $\exp(-\sqrt{x^2/a_x^2 + y^2/a_y^2})$ gives $\varepsilon_{00} = \alpha \epsilon_B \log^2 \eta$, where $\alpha = 1/\pi$ and $\alpha = 4/\pi^2$, correspondingly. These values of α do not strongly differ from $1/2$ found in the exactly solvable model (see Eq. (11)).

The binding energy of the lowest level ε_{00} essentially depends on the angle $\phi_{\mathbf{k}}$, while the angular dependence of the other levels touches only \mathbf{k} -dependent corrections to these levels. The corrections have essential-singular behaviors as functions of the parameter η different for odd and even states.

We have numerically calculated the binding energy of the lowest exciton level ε_{00} using the adiabatic approach. Figures 2 show the dependencies of ε_{00} on the exciton momentum. The calculations have been done by two steps: finding the energy terms and solving the Schrödinger equation in the y -direction.

It should be emphasized that full exciton energy $vk - \varepsilon_{mn}$ is always positive lying in the electron-hole continuum. However, the momentum conservation preserves the exciton from the decay, unless the scattering processes (weak by assumptions) are taken into account.

Statistics of graphene with excitons. Another unusual property of graphene is participation of excitons in equilibrium thermodynamics. The presence of excitonic states changes statistics and thermodynamic properties of graphene at the finite temperature T . Excitons are Bose-particles and the number of equilibrium excitons is indeterminate. Hence, in the Dirac point, they have a zero chemical potential. Excitons in graphene do not Bose-condensate due to their gapless spectrum. The exciton contribution to extensive thermodynamic parameters can be calculated by subtracting the contribution of free pair (that is included into the electron and hole contribu-

tion) from the bound pair. The correction to the energy is

$$\delta E = \frac{2}{\pi^2} \sum_{nm} \int d^2p \left(\frac{vp - \varepsilon_{nN}}{e^{\frac{vp - \varepsilon_{nN}}{k_B T}} - 1} - \frac{vp}{e^{\frac{vp}{k_B T}} - 1} \right), \quad (14)$$

where k_B is the Boltzmann constant. Taking into account the smallness of $\varepsilon_{nN} \ll vp$, we find the correction to the specific heat

$$C_{ex} \approx \alpha (g k_B T / v)^2 [c_1 \log^2 \theta / T - c_2 \log \theta / T + c_3], \quad (15)$$

where $\theta = 4\sqrt{3}v/k_B a$, $c_1 \approx 9.18$, $c_2 \approx 3.46$, $c_3 \approx 8.93$.

The contribution of bound pairs should be compared to that of the free electrons and holes $C_{e+h} = 3c_1(k_B T / 2v)^2$.

The specific heat of graphene at low temperature is mostly determined by the acoustic and softer vertical phonon modes. The acoustic phonons give contribution $C_{ph} \propto T^2/v_s^2$, where v_s is the sound velocity. This should be compared to the electrons and holes contribution in the Dirac point $\propto T^2/v^2$.

How to observe excitons in graphene? Let us discuss the possibility of observation of the indirect excitons in graphene. In a semiconductor with the energy gap excitons contribute to the absorption and, especially, the emission of light. The absence of the energy gap makes observation of excitons in graphene a different problem from the case of usual semiconductor, because exciton energies are distributed between zero and several tenth of eV that smears up the exciton resonance. The large momentum of indirect exciton blocks both direct optical excitation and recombination. However, the slow recombination and inter-valley relaxation preserve the excitons (when generated somehow) from the recombination or the decay. The frequency of photons with a small wave vectors, which can produce excitons, is very low. In that case, the solution can be found using a structure where electrons obtain an additional in-plane momentum from phonons with wave vectors \mathbf{K} , impurities, the artificial grating or the naturally ruffle of the graphene plane.

Phonon-assisted indirect exciton optical absorption has thresholds determined by one of phonon frequencies $\Omega_i(\mathbf{K})$, where i numerates the phonon type. Corresponding contribution to the absorption near the threshold $\Omega_i(\mathbf{K})$ is determined by the exciton density of states and is proportional to $(\omega - \Omega_i)\theta(\omega - \Omega_i)$, where ω is light frequency.

The other way perspective to observe excitons is based on a monolayer character of graphene. Being placed in vacuum, the graphene layer can serve as electron tube grid. This permits to study the scattering of vacuum electrons (forward or backward) on the graphene. The dependence of the energy loss maximum on the scattering angle gives the spectrum of the Bose excitation, in particular, excitons. To provide the necessary momentum transfer, the external electrons should have energy ~ 10 eV. The energy resolution of modern methods of low-energy electrons scattering is sufficient to resolve excitons with energies of some meV.

The electron subsystem specific heat can be isolated in dynamic experiments with quick electron heating by means of pulse voltage or light. In such conditions the electron temperature is separated from the phonon one and the electrical or optical responses will reflect the time evolution of the electron temperature connected with the electron cooling. Assuming quick establishment of the temperature equilibrium between electrons and excitons and slow establishment of the equilibrium between them and phonons one can find the ratio of temperature changes just after pulse δT_0 and after equalizing of phonon and electron subsystem temperatures δT_∞ : $\delta T_0/\delta T_\infty = 1 + C_{ph}/(C_{e+h} + C_{ex})$. This gives the thermodynamic way to observe excitons in graphene.

Discussion and conclusions. In the above consideration the many-body corrections have been neglected. Actually, the e-e interaction leads to the electron self-energy $\tilde{g}vk \ln(1/ka)$, $\tilde{g} = g/4 - g^2(5/6 - \ln 2) + O(g^3)$ ⁶. We have neglected these corrections, assuming that not only g , but typical $g \ln(1/pa)$ is less than unity. The presence of this logarithmic term strongly changes the behavior of the single-electron spectrum at small k and gives a negative contribution to M . However, this does not forbid the exciton absolutely. In fact, the interaction-induced correction to the inverse mass $1/m_{int} = -\tilde{g}v/k$ should be added to the warping correction. In a particular case of small interaction constant g , mass M becomes negative at low k and near the boundaries of the existence

sectors. This narrows the range of exciton existence and shifts it from the conic point.

Another remark concerns the renormalization of the dielectric constant χ , caused by the vacuum polarization of graphene⁷. The renormalization reduces the Coulomb interaction at large distance, as if the dielectric constant of external medium becomes logarithmically large. This fact improves the applicability of the weak-interaction model, even in the case of free-suspended graphene.

The excitons considered in the present paper arise near the conic points, unlike the saddle-point exciton states with energies about 5 eV studied in^{1-3,8-11}. The latter, in our opinion, correspond to the e-h scattering resonance, rather than bound states. The other investigations of exciton resonances is based on the electron spectrum reconstruction caused by large interaction constant^{14,15}. However, the possibility of gapless excitons in a system with small g considered here had not been studied earlier.

In conclusion, we have demonstrated the existence of moving indirect excitons in monolayer graphene and found their energies. The excitons are conditioned by the presence of the warping of the electron spectrum. The excitons spectrum has no gap. The many-body interaction corrections to the single-particle spectrum, in concurrence with warping, lead to the destruction of excitons with small wave vectors. However, the excitons survive if the interaction constant is small.

This research has been supported in part by the grants of RFBR No 11-02-00730 and 11-02-12142.

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